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APPLICANT : ASAHI GLASS CO LTD;

INVENTOR : KIJIMUTA HITOSHI;

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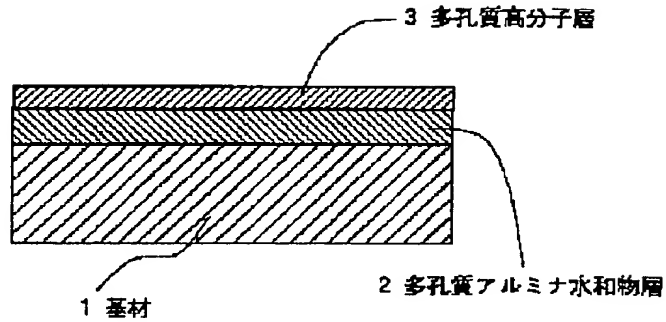
TITLE : RECORDED MATTER, PRODUCTION THEREOF AND RECORDING SHEET



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ABSTRACT : PURPOSE: To enhance the water resistance and durability of recorded matter by an ink jet printer and to keep high image quality for a long period of time.

CONSTITUTION: In a recording sheet wherein a base material 1, a porous alumina hydrate layer 2 and a porous high-polymer layer 3 are laminated, a dye is fixed to the porous alumina hydrate layer 2 through the porous high-polymer layer 3 by an ink jet printer to form an image and, thereafter, the porous-high polymer layer 3 is densified to form a transparent high-polymer film.

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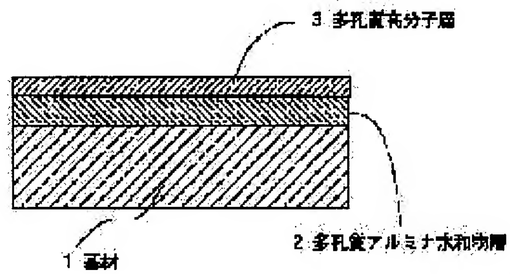
(54) **RECORDED MATTER, PRODUCTION THEREOF AND RECORDING SHEET**

(57)Abstract:
PURPOSE: To enhance the water resistance and durability of recorded matter by an ink jet printer and to keep high image quality for a long period of time.
CONSTITUTION: In a recording sheet wherein a base material 1, a porous alumina hydrate layer 2 and a porous high-polymer layer 3 are laminated, a dye is fixed to the porous alumina hydrate layer 2 through the porous high-polymer layer 3 by an ink jet printer to form an image and, thereafter, the porous-high polymer layer 3 is densified to form a transparent high-polymer film.



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CLAIMS

[Claim(s)]
[Claim 1] The record object which has the porosity hydrated-alumina layer in which the picture was formed and by which this porosity hydrated-alumina layer was covered with the transparent poly membrane with coloring matter on the base material.
[Claim 2] The record object of the claim 1 obtained by carrying out application dryness of the paint with which a transparent poly membrane forms the paint film which becomes transparence workmanship.
[Claim 3] The record object of a claim 1 with which a transparent poly membrane is obtained by precise-turning in a porosity macromolecule.
[Claim 4] The manufacture method of the record object which carries out application dryness of the paint which forms in this porosity hydrated-alumina layer the paint film which becomes transparence workmanship after fixing coloring matter to the porosity hydrated-alumina layer formed on the base material and forming a picture, and forms a transparent poly membrane.
[Claim 5] The manufacture method of the record object which turns precisely and forms a transparent poly membrane in the upper layer of a porosity hydrated-alumina layer by heat-treating a porosity macromolecule layer after forming a porosity macromolecule layer further, fixing coloring matter to a porosity hydrated-alumina layer through a porosity macromolecule layer and forming a picture on the porosity hydrated-alumina layer formed on the base material.
[Claim 6] The manufacture method of the record object of the claim 5 which forms a macromolecule latex by carrying out application dryness of the porosity macromolecule layer at a porosity hydrated-alumina layer.
[Claim 7] The manufacture method of the record object of the claim 6 which is mixed with a silica sol and applies a macromolecule latex.
[Claim 8] the claims 4-7 which use an ink jet printer for formation of a picture -- the manufacture method of the record object of any 1
[Claim 9] The record sheet for the ink jet printers with which the porosity macromolecule layer was formed on the porosity hydrated-alumina layer formed on the base material.
[Claim 10] The record sheet of the claim 9 which the different-species particle is distributing in a porosity macromolecule layer.
[Claim 11] The record sheet of the claims 9 or 10 whose porosity macromolecule layers are the application dry matters of a macromolecule latex.

[Translation done.]

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2.**** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] Especially this invention relates to the record object suitable for an ink jet printer, its manufacture method, and a record sheet about a record object, its manufacture method, and a record sheet.
[0002]
[Description of the Prior Art] The method of forming a picture and an especially full color picture is spreading quickly using recording methods, such as an ink-jet method, an electrostatic imprint method, and a sublimated type hot printing method. The target in such a method is a silver salt photograph, and it has been the technical problem of development how color-reproduction nature, picture density, gloss, water resistance, weatherability, etc. are brought especially close to a silver salt photograph.
[0003] Among these, an ink-jet method is a method which the ink drop injected at high speed is made to adhere to a recorded material, and records it from a nozzle, and has the features, like full-color-izing being easy and printing noise are low. By this recording method, since the ink used contains a lot of solvents, in order to obtain the high depth of shade, it is necessary to use a lot of ink. Moreover, if the following drop is injected before the first drop is absorbed, since an ink drop is injected continuously, the beading phenomenon which an ink drop unites and the dot of ink joins will arise, and a picture will be confused. Therefore, it is required for the record medium for ink jet printers that ink absorption capacity should be large and the rate of absorption of ink should be high.
[0004] For this reason, since absorptivity sufficient with ordinary paper or an ordinary film, coloring nature, and resolution are not obtained, the record medium which prepared the porous layer which consists of a hydrated alumina on the base material like JP,2-276670,A is proposed. If it records on such a record medium by the ink-jet method, it excels in the absorptivity of ink, and fixing nature, and it is reported that a picture with high resolution is acquired.
[0005]
[Problem(s) to be Solved by the Invention] By the ink-jet method, since the picture is formed with the coloring matter of solvent fusibility, about the water resistance of a record object, and weatherability, it is not necessarily enough, and there is a possibility that problems, such as fading, may occur, in the environment where it is exposed outdoors for a long period of time. Moreover, in the case of a porous ink acceptance layer, there is also a possibility that components other than ink may be adsorbed and a picture may become dirty. Resolution and coloring nature of this invention are good, and it aims at offering the record object excellent in water resistance, weatherability, and resistance to contamination.
[0006]
[Means for Solving the Problem] this invention has the porosity hydrated-alumina layer in which the picture was formed with coloring matter on the base material, and offers the record object by which this porosity hydrated-alumina layer was covered by the transparent poly membrane.
[0007] It is not limited especially as a base material, but various things can be used. Specifically, various plastics, such as a fluorine system resin, and papers, such as polyester, such as a polyethylene terephthalate, a polycarbonate, and ETFE, can be used suitably. Furthermore, a glass metallurgy group or a natural leather, artificial leather, cloth, etc. can be used. In these base materials, corona discharge processing, a under coat, etc. can also be processed for the purpose of raising the bond strength of a porosity hydrated alumina.
[0008] When transparent plastic film etc. is used as a base material, the transparent record object which can be used for OHP (over head projector) etc. is obtained. As a base material, when the opaque plastic film containing white pigments, paper, etc. are used, the record object which is equal to a silver salt photograph is obtained. Moreover, the depth of shade is high on artificial leather, cloth, etc., and a minute picture can be formed.
[0009] A porosity hydrated alumina has the desirable composition currently formed on the base material as a layer which combined the hydrated alumina with the binder. Since a record object with it is obtained using various kinds of recording methods in order that it may often adsorb coloring matter alternatively as a hydrated alumina, while absorptivity of a boehmite (aluminum2 O3 and nH2 O, n=1-1.5) is good, it is desirable. [the high depth of shade and] [clear]
[0010] When the porosity hydrated-alumina layer is formed in the porous base-material front face like paper or cloth, between a base material and a porosity hydrated-alumina layer, a clear interface may not not necessarily be. Namely, a portion with many hydrated aluminas should just be near the front face of a base material.
[0011] Since the pore structure consists of pore whose radius is 1-10nm substantially, and it has absorptivity sufficient when pore volume is 0.3 - 1.0 cc/g and is transparent, a porosity hydrated alumina is desirable. If the base material is transparent at this time, what also has a transparent record object will be obtained. When a base material is opaque, it is possible to give physical properties, such as absorptivity needed without spoiling the texture of a base material. It is still more desirable when the average pore radius of a porosity hydrated alumina is 3-7nm in addition to these physical properties. In addition, measurement of a pore volume distribution is based on a nitrogen adsorption-and-desorption method.
[0012] In order to form the porosity hydrated-alumina layer which has the above pore structures, it is desirable to add a binder to an alumina sol preferably, to consider as the shape of a slurry, to apply on a base material using a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a comma coating machine, etc., and to

adopt the method of drying.
[0013] As a binder, the organic substance, such as starch, its denaturation object, polyvinyl alcohol and its denaturation object, an SBR latex, an NBR latex, a hydroxy cellulose, and a polyvinyl pyrrolidone, can be used. Since it has a possibility that the intensity of a porosity hydrated-alumina layer may become inadequate when there is little amount of the binder used, and it has a possibility that the absorbed dose of ink and the amount of support of coloring matter may become low when there is conversely, about 5 - 50% of the weight of its hydrated alumina is desirable. [too much]
[0014] Since porosity hydrated-alumina layer thickness has a possibility that coloring matter cannot be supported enough but only the low printed matter of the depth of shade may be obtained when it is too thin, it is not desirable. Conversely, since the intensity of a porous layer falls or there is a possibility that transparency may decrease and the transparency or texture of printed matter may be spoiled when too thick, it is not desirable. The thickness with a desirable porosity hydrated-alumina layer is 1-50 micrometers.
[0015] With the transparent poly membrane in this invention, it is formed in the front face of the above-mentioned porosity hydrated-alumina layer, and this is covered. This transparent poly membrane has the effect which raises the water resistance of a picture, and weatherability. Transparence means that the picture formed in the porosity hydrated alumina can observe through a poly membrane here. Although it is desirable that it is colorlessness, you may color in order to give design nature. Especially the quality of the material of a transparent poly membrane is not limited, but can use various polymeric materials. Moreover, in the range which does not spoil transparency, even if the filler etc. is blended, it does not interfere.
[0016] The thickness of a transparent poly membrane has desirable 0.5-30 micrometers. When the thickness of a transparent poly membrane does not fulfill 0.5 micrometers, the effect of water resistance and weatherproof improvement is not enough, and since there is a possibility that quality of image may deteriorate by the manifestation of the interference color, it is not desirable. Since the effect of more than it, water resistance, and weatherproof improvement not only does not increase, but quality of image deteriorates with a concealment of a poly membrane or there is a possibility that peeling of a poly membrane and curl of a record object may occur when the thickness of a transparent poly membrane exceeds 30 micrometers, it is not desirable. The more desirable thickness of a transparent poly membrane is 2-10 micrometers.
[0017] The method of applying the paint which does not contain a pigment component in a porosity hydrated alumina substantially after image formation, i.e., the paint which becomes a transparence result, as an example of a means to form a transparent poly membrane is mentioned. As a paint, various things, such as an oil paint, a fiber system derivative paint, synthetic coating material, and a fluororesin paint, can be used. It is the point which make image formation spread and does not make [it is / a picture / sufficient for and] it it especially to what used water color ink, and the paint which uses oily solvents, such as an oil paint, is desirable.
[0018] As for the resinous principle in a paint, it is desirable that it is 3 - 30 % of the weight. when not filling the resinous principle in a paint to 3% of the weight, the transparent poly membrane formed is thin and the effect of water resistance and weatherproof improvement is enough -- since there is a possibility of it not coming out and producing deterioration of the quality of image by the manifestation of the interference color, it is not desirable On the contrary, since the viscosity of a paint rises, a uniform application becomes difficult, when the resinous principle in a paint exceeds 30 % of the weight and there is a possibility that quality of image may deteriorate, it is not desirable. Since the solvent in a paint is absorbed by the porosity hydrated alumina and viscosity rises at the time of an application in order to form a paint film in a porosity front face especially in the case of this invention, an application becomes difficult when a resinous principle exceeds 30 % of the weight.
[0019] Especially as for the method of application of a paint, brush coating, spray coating, roller coating, etc. are not limited. An air drying is sufficient as dryness and it may be heated if needed.
[0020] After recording with an ink jet printer etc. as means forming of a transparent poly membrane using the record sheet which formed the porosity macromolecule layer beforehand on the porosity hydrated-alumina layer on a base material in addition to the above applying methods, the method of turning a porosity macromolecule layer precisely and forming a transparent poly membrane on a porosity hydrated-alumina layer is also employable. At this time, ink permeates to a porosity hydrated alumina through a porosity macromolecule layer, and a hydrated alumina is fixed to it, and it forms a picture. As a means of precise-izing of a porosity macromolecule layer, heat-treatment is desirable.
[0021] An example of the record sheet used for this method is shown in drawing 1 . The porosity hydrated-alumina layer 2 is formed in the base material 1, and the laminating of the porosity macromolecule layer 3 is carried out further. When using such a record sheet, even if it does not use a paint etc. after record, there is an advantage that the record object which the transparent poly membrane formed can be obtained.
[0022] As for a porosity macromolecule layer, it is desirable to carry out application dryness and to form a macromolecule latex on a porosity hydrated-alumina layer. As a macromolecule latex, it is independent, or a PVC latex, an SBR latex, an NBR latex, etc. can be mixed and used.
[0023] As for a macromolecule latex, it is desirable that it is 0.05-0.5 micrometers of mean particle diameters. When the mean particle diameter of a macromolecule latex does not fulfill 0.05 micrometers, the good porosity macromolecule layer of absorptivity and permeability of ink is not formed, enough, ink permeates, a porosity hydrated-alumina layer is not fixed to it, and a desired picture cannot be formed. When the mean particle diameter of a macromolecule latex exceeds 0.5 micrometers, there is a possibility that the dot of ink may become uneven and the fall of a picture may arise. A mean particle diameter more desirable than a macromolecule latex is 0.08-0.3 micrometers.
[0024] As for the coat formation minimum temperature of a macromolecule latex, it is desirable that it is in the range of 50-150 degrees C. When the coat formation minimum temperature heats the paint film of a macromolecule latex, it is minimum temperature which can coat-ize this uniformly. In this invention, although it does not become a precise coat in order to make it a porosity macromolecule layer after applying a macromolecule latex, it is necessary to carry out stoving to a grade with a fixed mechanical strength on conditions which a latex particle combines. If it is difficult to obtain a porosity macromolecule layer that it is easy to become a precise coat and it tends to prevent this in case a macromolecule latex is applied and it dries, when the coat formation minimum temperature does not fulfill 50 degrees C, the drying time will become long, and since it is not industrial, it is not desirable. Since it is necessary to make high heat treatment temperature after image formation and there is a problem of the thermal denaturation of decomposition of a macromolecule, the problem

of coloring, a base material, or coloring matter when the coat formation minimum temperature exceeds 150 degrees C, it is not desirable. The more desirable coat formation minimum temperature is 65-130 degrees C.
[0025] Porosity macromolecule layer thickness has desirable 0.1-10 micrometers. when thickness does not fulfill 0.1 micrometers, the effect of the improvement in waterproof weatherability when coat-izing is enough -- since there is a possibility of it not coming out and causing deterioration of the quality of image by the manifestation of the interference color, it is not desirable Since the absorptivity of ink falls, or quality of image deteriorates when a crack occurred and coat-izes or there is a possibility that the effect of the improvement in waterproof weatherability may not occur when thickness exceeds 10 micrometers, it is not desirable. 0.3-5 micrometers of more desirable thickness of a porosity macromolecule layer are 0.5-3 micrometers especially preferably.
[0026] Although especially the solid-content concentration of a macromolecule latex is not restricted, the latex of 1 - 50% of the weight of solid-content concentration can be used suitably. In addition, to a macromolecule latex, you may add other macromolecule components with a binder operation.
[0027] Especially the method of application of a macromolecule latex is not restricted, but can use a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a gravure coating machine, etc. It is desirable to perform dryness at the temperature below the coat formation minimum temperature of the macromolecule latex to be used.

[0028] Thus, when a picture is formed in the formed record sheet with the upper shell ink jet printer of a porosity macromolecule layer, ink reaches it to a hydrated-alumina layer through a porosity macromolecule layer. Since the adsorptivity of a hydrated alumina of the coloring matter in ink is high, a picture is substantially formed in the portion of a hydrated-alumina layer. Then, if a porosity macromolecule layer is made precise with heat treatment etc., it will come to act as a protective layer of the coloring matter to which the rarefaction was carried out and the hydrated-alumina layer was fixed. That heat treatment should just be more than the coat formation minimum temperature of a latex, especially a heating means is not restricted but hot blast, an iron, etc. can be used for it.
[0029] Furthermore, since the beading-proof property at the time of recording with an ink jet printer improves remarkably when the different-species particle is distributing to the macromolecule porous layer, it is desirable. An inorganic particle is desirable as a particle and a silica particle is specifically suitable. If a size and loadings are suitable for this particle, when a macromolecule porous layer is turned precisely, it will not spoil transparency.
[0030] When using a silica particle, as a diameter of a particle, about 0.03-0.3 micrometers is suitable. Since the above-mentioned effect is not discovered enough when a particle diameter does not fulfill 0.03 micrometers, it is not desirable. Since there is a possibility of transparency being insufficient and degrading quality of image when a particle diameter exceeds 0.3 micrometers, and a macromolecule porous membrane is turned precisely, it is not desirable. A more desirable particle diameter is 0.05-0.1 micrometers.
[0031] When using a silica particle, as for the mixed rate of a macromolecule and a silica particle in a macromolecule porous layer, it is desirable that a silica particle is 50 or less % of the weight to the total quantity of a macromolecule and a silica particle. Since it is difficult to carry out the precise rarefaction after record when a silica particle exceeds 50 % of the weight, it is not desirable. The silica particle of a more desirable rate is 15 - 40 % of the weight to the total quantity of a macromolecule and a silica particle.
[0032] The method of adjusting the coating liquid which mixed the silica sol to a macromolecule latex as a method of obtaining the macromolecule porous layer of composition of the silica particle having distributed uniformly, and carrying out application dryness of this on a hydrated-alumina layer is suitable. In this case, a silica particle also has the effect which suppresses generating of a crack in the case of formation of a macromolecule porous layer. The method of application etc. can adopt the same thing as a latex independent case. The thickness of a macromolecule porous layer is the same as a latex independent case, and good.
[0033] In case the precise rarefaction is carried out even if it blends different-species particles, such as a silica, and does not carry out when a macromolecule latex is applied and a porosity macromolecule layer is formed, layer thickness hardly changes. That is, although it is porosity, it is thought that the macromolecule layer with small pore volume is formed. For this reason, when it heats, it is thought that a particle welds easily and carries out the rarefaction.
[0034] The glossiness of a record object improves by forming a transparent poly membrane. When paper is especially used as a base material, and glossiness improves, improvement in quality of image is also found. Since it has gloss good from the first when plastic film smooth as a base material is used, glossiness becomes high too much, depending on the use of a record object, texture is conversely bad and there may be things. In such a case, lusterless processing can also be performed to a transparent poly membrane.
[0035] Although the record object of this invention is suitable when recording especially using an ink jet printer, it is applicable to other recording methods recorded using coloring matter.
[0036]
[Function] They are the oxygen in air, ozone, and NOx in that coloring matter touches water in this invention when a transparent poly membrane covers a porosity hydrated alumina ****. It reacts, or prevents volatilizing and has the function which covers ultraviolet rays further. Since the transparent macromolecule layer side of a hydrated-alumina layer is mostly fixed to coloring matter even if it penetrates air etc. like [in case base materials are paper and cloth], an effect is demonstrated similarly.
[0037]
[Example]
32g of 6.2 % of the weight solution of polyvinyl alcohol was mixed with alumina-sol of 18 % of the weight of solid contents compounded by hydrolysis and amalgam-decomposition method of example 1 aluminum alkoxide 100g, and it considered as coating liquid. On the polyethylene-terephthalate film (a white film, 125-micrometer **), coating of this coating liquid was carried out using the bar coating machine so that the coating thickness after dryness might be set to 30 micrometers. It heat-treated at 140 degrees C, and the record sheet took after drying this.
[0038] After using the ink jet printer (CJ[by Canon, Inc.]-10 type) for this record sheet and forming a picture in it, what diluted the synthetic coating material (urethane varnish by Kansai Paint Co., Ltd.) of an urethane system with petroleum

system thinner to 20 % of the weight of pitches was applied with the brush, was air-dried, the transparent poly membrane with a thickness of about 5 micrometers was formed, and the record object was obtained.
[0039] After recording on the record sheet of example 2 example 1 with an ink jet printer similarly, n-butanol solution of 5 % of the weight of polyvinyl butyral resin was used as the paint, application dryness was carried out like the example 1, the transparent poly membrane with a thickness of about 5 micrometers was formed, and the record object was obtained.
[0040] On the record sheet of example 3 example 1, it applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 2 micrometers by 0.1 micrometers of mean particle diameters in the PVC latex (the Nippon Zeon Co., Ltd. make, tradename G351) of 10 % of the weight of solid contents, and stoving was carried out in 60-degree C atmosphere, and the porosity poly membrane was formed.
[0041] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (100 degrees C), the porosity poly membrane was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 2 micrometers.
[0042] On the record sheet of example 4 example 1, it applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 1 micrometer by 0.12 micrometers of mean particle diameters in the SBR latex (the Nippon Zeon Co., Ltd. make, tradename NIPORU LX382) of 5 % of the weight of solid contents, and stoving was carried out in 90-degree C atmosphere, and the porosity poly membrane was formed.
[0043] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (130 degrees C), the porosity poly membrane was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 1 micrometer.
[0044] The silica sol (catalyst Chemicals industrial incorporated company make, tradename KATAROIDO SI-80P) of 0.08 micrometers of mean particle diameters was mixed with the SBR latex (the Nippon Zeon Co., Ltd. make, tradename NIPORU LX382) of 5 % of the weight of solid contents at a rate of 80:20 by 0.12 micrometers of example 5 mean particle diameters at the solid-content weight ratio, and coating liquid of the 10 % of the weight of the total solid-content concentration was prepared. With time, this mixed coating liquid was not seen but that of especially change was stable. On the record sheet of an example 1, this coating liquid was applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 1.5 micrometers, stoving was carried out in 90-degree C atmosphere, and the porosity poly membrane which the silica particle contained was formed.
[0045] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (130 degrees C), the porosity poly membrane was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 1.5 micrometers.
[0046] the example of printing -- water resistance and weatherability were evaluated as follows about the record object of these A result is shown in Table 1 by making into the example of comparison the record object obtained similarly except not forming a transparent poly membrane. water resistance -- a record object -- dead water -- it was immersed in inside for one day, and ** and the thing to which quality of image fell remarkably were evaluated for what has bleeding O and a little in some which are completely changeless as x Weatherability exposed the record object indoors for three months, and evaluated as x ** and the thing which changed brown for what discolored O and a little what does not change at all about the discoloration degree (fade : black shell brown) of the black Records Department.
[0047]
[Table 1]

	耐水性	耐候性
実施例 1	○	○
実施例 2	○	○
実施例 3	○	○
実施例 4	○	○
実施例 5	○	○
比較例	△	×

[0048]
[Effect of the Invention] The record object of this invention is excellent in water resistance and weatherability, and has the preservation stability which maintains high definition over a long period of time. Especially, it is suitable to the record using water color ink. Moreover, the record method of this invention also has the effect that desirable gloss can be given to a record object.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] Especially this invention relates to the record object suitable for an ink jet printer, its manufacture method, and a record sheet about a record object, its manufacture method, and a record sheet.

[Translation done.]

PRIOR ART

[Description of the Prior Art] The method of forming a picture and an especially full color picture is spreading quickly using recording methods, such as an ink-jet method, an electrostatic imprint method, and a sublimated type hot printing method. The target in such a method is a silver salt photograph, and it has been the technical problem of development how color-reproduction nature, picture density, gloss, water resistance, weatherability, etc. are brought especially close to a silver salt photograph.

[0003] Among these, an ink-jet method is a method which the ink drop injected at high speed is made to adhere to a recorded material, and records it from a nozzle, and has the features, like full-color-izing being easy and printing noise are low. By this recording method, since the ink used contains a lot of solvents, in order to obtain the high depth of shade, it is necessary to use a lot of ink. Moreover, if the following drop is injected before the first drop is absorbed, since an ink drop is injected continuously, the beading phenomenon which an ink drop unites and the dot of ink joins will arise, and a picture will be confused. Therefore, it is required for the record medium for ink jet printers that ink absorption capacity should be large and the rate of absorption of ink should be high.

[0004] For this reason, since absorptivity sufficient with ordinary paper or an ordinary film, coloring nature, and resolution are not obtained, the record medium which prepared the porous layer which consists of a hydrated alumina on the base material like JP,2-276670,A is proposed. If it records on such a record medium by the ink-jet method, it excels in the absorptivity of ink, and fixing nature, and it is reported that a picture with high resolution is acquired.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] The record object of this invention is excellent in water resistance and weatherability, and has the preservation stability which maintains high definition over a long period of time. Especially, it is suitable to the record using water color ink. Moreover, the record method of this invention also has the effect that desirable gloss can be given to a record object.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the ink-jet method, since the picture is formed with the coloring matter of solvent fusibility, about the water resistance of a record object, and weatherability, it is not necessarily enough, and there is a possibility that problems, such as fading, may occur, in the environment where it is exposed outdoors for a long period of time. Moreover, in the case of a porous ink acceptance layer, there is also a possibility that components other than ink may be adsorbed and a picture may become dirty. Resolution and coloring nature of this invention are good, and it aims at offering the record object excellent in water resistance, weatherability, and resistance to contamination.

[Translation done.]

MEANS

[Means for Solving the Problem] this invention has the porosity hydrated-alumina layer in which the picture was formed with coloring matter on the base material, and offers the record object by which this porosity hydrated-alumina layer was covered by the transparent poly membrane.
[0007] It is not limited especially as a base material, but various things can be used. Specifically, various plastics, such as a fluorine system resin, and papers, such as polyester, such as a polyethylene terephthalate, a polycarbonate, and ETFE, can be used suitably. Furthermore, a glass metallurgy group or a natural leather, artificial leather, cloth, etc. can be used. In these base materials, corona discharge processing, a under coat, etc. can also be processed for the purpose of raising the bond strength of a porosity hydrated alumina.
[0008] When transparent plastic film etc. is used as a base material, the transparent record object which can be used for OHP (over head projector) etc. is obtained. As a base material, when the opaque plastic film containing white pigments, paper, etc. are used, the record object which is equal to a silver salt photograph is obtained. Moreover, the depth of shade is high on artificial leather, cloth, etc., and a minute picture can be formed.
[0009] A porosity hydrated alumina has the desirable composition currently formed on the base material as a layer which combined the hydrated alumina with the binder. Since a record object with it is obtained using various kinds of recording methods in order that it may often adsorb coloring matter alternatively as a hydrated alumina, while absorptivity of a boehmite (aluminum2 O3 and nH2 O, n=1-1.5) is good, it is desirable. [the high depth of shade and] [clear]
[0010] When the porosity hydrated-alumina layer is formed in the porous base-material front face like paper or cloth, between a base material and a porosity hydrated-alumina layer, a clear interface may not not necessarily be. Namely, a portion with many hydrated aluminas should just be near the front face of a base material.
[0011] Since the pore structure consists of pore whose radius is 1-10nm substantially, and it has absorptivity sufficient when pore volume is 0.3 - 1.0 cc/g and is transparent, a porosity hydrated alumina is desirable. If the base material is transparent at this time, what also has a transparent record object will be obtained. When a base material is opaque, it is possible to give physical properties, such as absorptivity needed without spoiling the texture of a base material. It is still more desirable when the average pore radius of a porosity hydrated alumina is 3-7nm in addition to these physical properties. In addition, measurement of a pore volume distribution is based on a nitrogen adsorption-and-desorption method.
[0012] In order to form the porosity hydrated-alumina layer which has the above pore structures, it is desirable to add a binder to an alumina sol preferably, to consider as the shape of a slurry, to apply on a base material using a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a comma coating machine, etc., and to adopt the method of drying.
[0013] As a binder, the organic substance, such as starch, its denaturation object, polyvinyl alcohol and its denaturation object, an SBR latex, an NBR latex, a hydroxy cellulose, and a polyvinyl pyrrolidone, can be used. Since it has a possibility that the intensity of a porosity hydrated-alumina layer may become inadequate when there is little amount of the binder used, and it has a possibility that the absorbed dose of ink and the amount of support of coloring matter may become low when there is conversely, about 5 - 50% of the weight of its hydrated alumina is desirable. [too much]
[0014] Since porosity hydrated-alumina layer thickness has a possibility that coloring matter cannot be supported enough but only the low printed matter of the depth of shade may be obtained when it is too thin, it is not desirable. Conversely, since the intensity of a porous layer falls or there is a possibility that transparency may decrease and the transparency or texture of printed matter may be spoiled when too thick, it is not desirable. The thickness with a desirable porosity hydrated-alumina layer is 1-50 micrometers.
[0015] With the transparent poly membrane in this invention, it is formed in the front face of the above-mentioned porosity hydrated-alumina layer, and this is covered. This transparent poly membrane has the effect which raises the water resistance of a picture, and weatherability. Transparence means that the picture formed in the porosity hydrated alumina can observe through a poly membrane here. Although it is desirable that it is colorlessness, you may color in order to give design nature. Especially the quality of the material of a transparent poly membrane is not limited, but can use various polymeric materials. Moreover, in the range which does not spoil transparency, even if the filler etc. is blended, it does not interfere.
[0016] The thickness of a transparent poly membrane has desirable 0.5-30 micrometers. When the thickness of a transparent poly membrane does not fulfill 0.5 micrometers, the effect of water resistance and weatherproof improvement is not enough, and since there is a possibility that quality of image may deteriorate by the manifestation of the interference color, it is not desirable. Since the effect of more than it, water resistance, and weatherproof improvement not only does not increase, but quality of image deteriorates with a concealment of a poly membrane or there is a possibility that peeling of a poly membrane and curl of a record object may occur when the thickness of a transparent poly membrane exceeds 30 micrometers, it is not desirable. The more desirable thickness of a transparent poly membrane is 2-10 micrometers.
[0017] The method of applying the paint which does not contain a pigment component in a porosity hydrated alumina substantially after image formation, i.e., the paint which becomes a transparence result, as an example of a means to form a transparent poly membrane is mentioned. As a paint, various things, such as an oil paint, a fiber system derivative paint, synthetic coating material, and a fluororesin paint, can be used. It is the point which make image formation spread and does not make [it is / a picture / sufficient for and] it it especially to what used water color ink, and the paint which uses oily

solvents, such as an oil paint, is desirable.
[0018] As for the resinous principle in a paint, it is desirable that it is 3 - 30 % of the weight. when not filling the resinous principle in a paint to 3% of the weight, the transparent poly membrane formed is thin and the effect of water resistance and weatherproof improvement is enough -- since there is a possibility of it not coming out and producing deterioration of the quality of image by the manifestation of the interference color, it is not desirable On the contrary, since the viscosity of a paint rises, a uniform application becomes difficult, when the resinous principle in a paint exceeds 30 % of the weight and there is a possibility that quality of image may deteriorate, it is not desirable. Since the solvent in a paint is absorbed by the porosity hydrated alumina and viscosity rises at the time of an application in order to form a paint film in a porosity front face especially in the case of this invention, an application becomes difficult when a resinous principle exceeds 30 % of the weight.
[0019] Especially as for the method of application of a paint, brush coating, spray coating, roller coating, etc. are not limited. An air drying is sufficient as dryness and it may be heated if needed.
[0020] After recording with an ink jet printer etc. as means forming of a transparent poly membrane using the record sheet which formed the porosity macromolecule layer beforehand on the porosity hydrated-alumina layer on a base material in addition to the above applying methods, the method of turning a porosity macromolecule layer precisely and forming a transparent poly membrane on a porosity hydrated-alumina layer is also employable. At this time, ink permeates to a porosity hydrated alumina through a porosity macromolecule layer, and a hydrated alumina is fixed to it, and it forms a picture. As a means of precise-izing of a porosity macromolecule layer, heat-treatment is desirable.
[0021] An example of the record sheet used for this method is shown in drawing 1 . The porosity hydrated-alumina layer 2 is formed in the base material 1, and the laminating of the porosity macromolecule layer 3 is carried out further. When using such a record sheet, even if it does not use a paint etc. after record, there is an advantage that the record object which the transparent poly membrane formed can be obtained.
[0022] As for a porosity macromolecule layer, it is desirable to carry out application dryness and to form a macromolecule latex on a porosity hydrated-alumina layer. As a macromolecule latex, it is independent, or a PVC latex, an SBR latex, an NBR latex, etc. can be mixed and used.
[0023] As for a macromolecule latex, it is desirable that it is 0.05-0.5 micrometers of mean particle diameters. When the mean particle diameter of a macromolecule latex does not fulfill 0.05 micrometers, the good porosity macromolecule layer of absorptivity and permeability of ink is not formed, enough, ink permeates, a porosity hydrated-alumina layer is not fixed to it, and a desired picture cannot be formed. When the mean particle diameter of a macromolecule latex exceeds 0.5 micrometers, there is a possibility that the dot of ink may become uneven and the fall of a picture may arise. A mean particle diameter more desirable than a macromolecule latex is 0.08-0.3 micrometers.
[0024] As for the coat formation minimum temperature of a macromolecule latex, it is desirable that it is in the range of 50-150 degrees C. When the coat formation minimum temperature heats the paint film of a macromolecule latex, it is minimum temperature which can coat-ize this uniformly. In this invention, although it does not become a precise coat in order to make it a porosity macromolecule layer after applying a macromolecule latex, it is necessary to carry out stoving to a grade with a fixed mechanical strength on conditions which a latex particle combines. If it is difficult to obtain a porosity macromolecule layer that it is easy to become a precise coat and it tends to prevent this in case a macromolecule latex is applied and it dries, when the coat formation minimum temperature does not fulfill 50 degrees C, the drying time will become long, and since it is not industrial, it is not desirable. Since it is necessary to make high heat treatment temperature after image formation and there is a problem of the thermal denaturation of decomposition of a macromolecule, the problem of coloring, a base material, or coloring matter when the coat formation minimum temperature exceeds 150 degrees C, it is not desirable. The more desirable coat formation minimum temperature is 65-130 degrees C.
[0025] Porosity macromolecule layer thickness has desirable 0.1-10 micrometers. when thickness does not fulfill 0.1 micrometers, the effect of the improvement in waterproof weatherability when coat-izing is enough -- since there is a possibility of it not coming out and causing deterioration of the quality of image by the manifestation of the interference color, it is not desirable Since the absorptivity of ink falls, or quality of image deteriorates when a crack occurred and coat-izes or there is a possibility that the effect of the improvement in waterproof weatherability may not occur when thickness exceeds 10 micrometers, it is not desirable. 0.3-5 micrometers of more desirable thickness of a porosity macromolecule layer are 0.5-3 micrometers especially preferably.
[0026] Although especially the solid-content concentration of a macromolecule latex is not restricted, the latex of 1 - 50% of the weight of solid-content concentration can be used suitably. In addition, to a macromolecule latex, you may add other macromolecule components with a binder operation.
[0027] Especially the method of application of a macromolecule latex is not restricted, but can use a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a gravure coating machine, etc. It is desirable to perform dryness at the temperature below the coat formation minimum temperature of the macromolecule latex to be used.

[0028] Thus, when a picture is formed in the formed record sheet with the upper shell ink jet printer of a porosity macromolecule layer, ink reaches it to a hydrated-alumina layer through a porosity macromolecule layer. Since the adsorptivity of a hydrated alumina of the coloring matter in ink is high, a picture is substantially formed in the portion of a hydrated-alumina layer. Then, if a porosity macromolecule layer is made precise with heat treatment etc., it will come to act as a protective layer of the coloring matter to which the rarefaction was carried out and the hydrated-alumina layer was fixed. That heat treatment should just be more than the coat formation minimum temperature of a latex, especially a heating means is not restricted but hot blast, an iron, etc. can be used for it.
[0029] Furthermore, since the beading-proof property at the time of recording with an ink jet printer improves remarkably when the different-species particle is distributing to the macromolecule porous layer, it is desirable. An inorganic particle is desirable as a particle and a silica particle is specifically suitable. If a size and loadings are suitable for this particle, when a macromolecule porous layer is turned precisely, it will not spoil transparency.
[0030] When using a silica particle, as a diameter of a particle, about 0.03-0.3 micrometers is suitable. Since the above-mentioned effect is not discovered enough when a particle diameter does not fulfill 0.03 micrometers, it is not

desirable. Since there is a possibility of transparency being insufficient and degrading quality of image when a particle diameter exceeds 0.3 micrometers, and a macromolecule porous membrane is turned precisely, it is not desirable. A more desirable particle diameter is 0.05-0.1 micrometers.
[0031] When using a silica particle, as for the mixed rate of a macromolecule and a silica particle in a macromolecule porous layer, it is desirable that a silica particle is 50 or less % of the weight to the total quantity of a macromolecule and a silica particle. Since it is difficult after record to form precise transparence when a silica particle exceeds 50 % of the weight, it is not desirable. The silica particle of a more desirable rate is 15 - 40 % of the weight to the total quantity of a macromolecule and a silica particle.
[0032] The method of adjusting the coating liquid which mixed the silica sol to a macromolecule latex as a method of obtaining the macromolecule porous layer of composition of the silica particle having distributed uniformly, and carrying out application dryness of this on a hydrated-alumina layer is suitable. In this case, a silica particle also has the effect which suppresses generating of a crack in the case of formation of a macromolecule porous layer. The method of application etc. can adopt the same thing as a latex independent case. The thickness of a macromolecule porous layer is the same as a latex independent case, and good.
[0033] In case precise transparence is formed even if it blends different-species particles, such as a silica, and does not carry out when a macromolecule latex is applied and a porosity macromolecule layer is formed, layer thickness hardly changes. That is, although it is porosity, it is thought that the macromolecule layer with small pore volume is formed. For this reason, when it heats, it is thought that a particle welds easily and transparence-izes.
[0034] The glossiness of a record object improves by forming a transparent poly membrane. When paper is especially used as a base material, and glossiness improves, improvement in quality of image is also found. Since it has gloss good from the first when plastic film smooth as a base material is used, glossiness becomes high too much, depending on the use of a record object, texture is conversely bad and there may be things. In such a case, lusterless processing can also be performed to a transparent poly membrane.
[0035] Although the record object of this invention is suitable when recording especially using an ink jet printer, it is applicable to other recording methods recorded using coloring matter.

[Translation done.]

OPERATION

[Function] They are the oxygen in air, ozone, and NOx in that coloring matter touches water in this invention when a transparent poly membrane covers a porosity hydrated alumina ****. It reacts, or prevents volatilizing and has the function which covers ultraviolet rays further. Since the transparent macromolecule layer side of a hydrated-alumina layer is mostly fixed to coloring matter even if it penetrates air etc. like [in case base materials are paper and cloth], an effect is demonstrated similarly.

[Translation done.]

EXAMPLE

[Example]
32g of 6.2 % of the weight solution of polyvinyl alcohol was mixed with alumina-sol of 18 % of the weight of solid contents compounded by hydrolysis and amalgam-decomposition method of example 1 aluminum alkoxide 100g, and it considered as coating liquid. On the polyethylene-terephthalate film (a white film, 125-micrometer **), coating of this coating liquid was carried out using the bar coating machine so that the coating thickness after dryness might be set to 30 micrometers. It heat-treated at 140 degrees C, and the record sheet took after drying this.
[0038] After using the ink jet printer (CJ[by Canon, Inc.]-10 type) for this record sheet and forming a picture in it, what diluted the synthetic coating material (urethane varnish by Kansai Paint Co., Ltd.) of an urethane system with petroleum system thinner to 20 % of the weight of pitches was applied with the brush, was air-dried, the transparent poly membrane with a thickness of about 5 micrometers was formed, and the record object was obtained.
[0039] After recording on the record sheet of example 2 example 1 with an ink jet printer similarly, n-butanol solution of 5 % of the weight of polyvinyl butyral resin was used as the paint, application dryness was carried out like the example 1, the transparent poly membrane with a thickness of about 5 micrometers was formed, and the record object was obtained.
[0040] On the record sheet of example 3 example 1, it applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 2 micrometers by 0.1 micrometers of mean particle diameters in the PVC latex (the Nippon Zeon Co., Ltd. make, tradename G351) of 10 % of the weight of solid contents, and stoving was carried out in 60-degree C atmosphere, and the porosity poly membrane was formed.
[0041] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (100 degrees C), the porosity poly membrane was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 2 micrometers.
[0042] On the record sheet of example 4 example 1, it applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 1 micrometer by 0.12 micrometers of mean particle diameters in the SBR latex (the Nippon Zeon Co., Ltd. make, tradename NIPORU LX382) of 5 % of the weight of solid contents, and stoving was carried out in 90-degree C atmosphere, and the porosity poly membrane was formed.
[0043] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (130 degrees C), the porosity poly membrane was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 1 micrometer.
[0044] The silica sol (catalyst Chemicals industrial incorporated company make, tradename KATAROIDO SI-80P) of 0.08 micrometers of mean particle diameters was mixed with the SBR latex (the Nippon Zeon Co., Ltd. make, tradename NIPORU LX382) of 5 % of the weight of solid contents at a rate of 80:20 by 0.12 micrometers of example 5 mean particle diameters at the solid-content weight ratio, and coating liquid of the 10 % of the weight of the total solid-content concentration was prepared. With time, this mixed coating liquid was not seen but that of especially change was stable. On the record sheet of an example 1, this coating liquid was applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 1.5 micrometers, stoving was carried out in 90-degree C atmosphere, and the porosity poly membrane which the silica particle contained was formed.
[0045] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (130 degrees C), the porosity poly membrane was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 1.5 micrometers.
[0046] the example of printing -- water resistance and weatherability were evaluated as follows about the record object of these A result is shown in Table 1 by making into the example of comparison the record object obtained similarly except not forming a transparent poly membrane. water resistance -- a record object -- dead water -- it was immersed in inside for one day, and ** and the thing to which quality of image fell remarkably were evaluated for what has bleeding O and a little in some which are completely changeless as x Weatherability exposed the record object indoors for three months, and evaluated as x ** and the thing which changed brown for what discolored O and a little what does not change at all about the discoloration degree (fade : black shell brown) of the black Records Department.
[0047]
[Table 1]

	耐水性	耐候性
実施例1	○	○
実施例2	○	○
実施例3	○	○
実施例4	○	○
実施例5	○	○
比較例	△	×

[Translation done.]

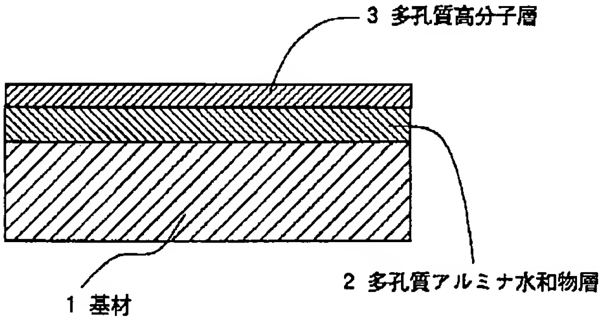
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Explanatory drawing showing the composition of one example of the record sheet of this invention
[Description of Notations]
1: Base material
2: Porosity hydrated-alumina layer
3: Porosity macromolecule layer

[Translation done.]

DRAWINGS

[Drawing 1]



[Translation done.]

CORRECTION or AMENDMENT

[Official Gazette Type] Printing of the amendment by the convention of 2 of Article 17 of patent law.
[Section partition] The 4th partition of the 2nd section.
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[FI]

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[Procedure revision]
[Filing Date] January 23, Heisei 13 (2001. 1.23)
[Procedure amendment 1]
[Document to be Amended] Specification.
[Item(s) to be Amended] Whole sentence.
[Method of Amendment] Change.
[Proposed Amendment]
[Document Name] Specification.
[Title of the Invention] A record object, its manufacture method, and a record sheet.
[Claim(s)]
[Claim 1] The record object which has the porosity hydrated-alumina layer in which the picture was formed and by which this porosity hydrated-alumina layer was covered with the transparent poly membrane with coloring matter on the base material.
[Claim 2] The record object according to claim 1 obtained by carrying out application dryness of the paint with which a transparent poly membrane forms the paint film which becomes transparence workmanship.
[Claim 3] The record object according to claim 1 with which a transparent poly membrane is obtained by precise-turning in a porosity macromolecule layer.
[Claim 4] The manufacture method of the record object which carries out application dryness of the paint which forms in this porosity hydrated-alumina layer the paint film which becomes transparence workmanship after fixing coloring matter to the porosity hydrated-alumina layer formed on the base material and forming a picture, and forms a transparent poly membrane.
[Claim 5] The manufacture method of the record object which turns precisely and forms a transparent poly membrane in the upper layer of a porosity hydrated-alumina layer by heat-treating a porosity macromolecule layer after forming a porosity macromolecule layer further, fixing coloring matter to a porosity hydrated-alumina layer through a porosity macromolecule layer and forming a picture on the porosity hydrated-alumina layer formed on the base material.
[Claim 6] The manufacture method of the record object according to claim 5 which forms a macromolecule latex by carrying out application dryness of the porosity macromolecule layer at a porosity hydrated-alumina layer.
[Claim 7] The manufacture method of the record object according to claim 6 which is mixed with a silica sol and applies a macromolecule latex.
[Claim 8] The record sheet for the ink jet printers with which the porosity macromolecule layer was formed on the porosity hydrated-alumina layer formed on the base material.
[Claim 9] The record sheet according to claim 9 which the different-species particle is distributing in a porosity macromolecule layer.
[Detailed Description of the Invention]
[0001]
[Industrial Application] Especially this invention relates to the record object suitable for an ink jet printer, its manufacture method, and a record sheet about a record object, its manufacture method, and a record sheet.
[0002]
[Description of the Prior Art] The method of forming a picture and an especially full color picture is spreading quickly using recording methods, such as an ink-jet method, an electrostatic imprint method, and a sublimated type hot printing method.

The target in such a method is a silver salt photograph, and it has been the technical problem of development how color-reproduction nature, picture density, gloss, water resistance, weatherability, etc. are brought especially close to a silver salt photograph.

[0003] Among these, an ink-jet method is a method which the ink drop injected at high speed is made to adhere to a recorded material, and records it from a nozzle, and has the features, like full-color-izing being easy and printing noise are low. By this recording method, since the ink used contains a lot of solvents, in order to obtain the high depth of shade, it is necessary to use a lot of ink. Moreover, if the following drop is injected before the first drop is absorbed, since an ink drop is injected continuously, the beading phenomenon which an ink drop unites and the dot of ink joins will arise, and a picture will be confused. Therefore, it is required for the record medium for ink jet printers that ink absorption capacity should be large and the rate of absorption of ink should be high.

[0004] For this reason, since absorptivity sufficient with ordinary paper or an ordinary film, coloring nature, and resolution are not obtained, the record medium which prepared the porous layer which consists of a hydrated alumina on the base material like JP,2-276670,A is proposed. If it records on such a record medium by the ink-jet method, it excels in the absorptivity of ink, and fixing nature, and it is reported that a picture with high resolution is acquired.

[0005]

[Problem(s) to be Solved by the Invention] By the ink-jet method, since the picture is formed with the coloring matter of solvent fusibility, about the water resistance of a record object, and weatherability, it is not necessarily enough, and there is a possibility that problems, such as fading, may occur, in the environment where it is exposed outdoors for a long period of time. Moreover, in the case of a porous ink acceptance layer, there is also a possibility that components other than ink may be adsorbed and a picture may become dirty. Resolution and coloring nature of this invention are good, and it aims at offering the record object excellent in water resistance, weatherability, and resistance to contamination.

[0006]

[Means for Solving the Problem] this invention has the porosity hydrated-alumina layer in which the picture was formed with coloring matter on the base material, and offers the record object by which this porosity hydrated-alumina layer was covered by the transparent poly membrane.

[0007] It is not limited especially as a base material, but various things can be used. Specifically, various plastics, such as a fluorine system resin, and papers, such as polyester, such as a polyethylene terephthalate, a polycarbonate, and ETFE, can be used suitably. Furthermore, glass, a metal, a natural leather, artificial leather, cloth, etc. can be used. In these base materials, corona discharge processing, a under coat, etc. can also be processed for the purpose of raising the bond strength of a porosity hydrated-alumina layer.

[0008] When transparent plastic film etc. is used as a base material, the transparent record object which can be used for OHP (over head projector) etc. is obtained. As a base material, when the opaque plastic film containing white pigments, paper, etc. are used, the record object which is equal to a silver salt photograph is obtained. Moreover, the depth of shade is high on artificial leather, cloth, etc., and a minute picture can be formed.

[0009] A porosity hydrated alumina has the desirable composition currently formed on the base material as a layer which combined the hydrated alumina with the binder. Since a record object with it is obtained using various kinds of recording methods in order that it may often adsorb coloring matter alternatively as a hydrated alumina, while absorptivity of a boehmite (aluminum2 O3 and nH2 O, n=1-1.5) is good, it is desirable. [the high depth of shade and] [clear]

[0010] When the porosity hydrated-alumina layer is formed in the porous base-material front face like paper or cloth, between a base material and a porosity hydrated-alumina layer, a clear interface may not not necessarily be. Namely, a portion with many hydrated aluminas should just be near the front face of a base material.

[0011] Since the pore structure consists of pore whose radius is 1-10nm substantially, and it has absorptivity sufficient when pore volume is 0.3 - 1.0 cc/g and is transparent, a porosity hydrated alumina is desirable. If the base material is transparent at this time, what also has a transparent record object will be obtained. When a base material is opaque, physical properties, such as absorptivity needed without spoiling the texture of a base material, can be given. It is still more desirable when the average pore radius of a porosity hydrated alumina is 3-7nm in addition to these physical properties. In addition, measurement of a pore volume distribution is based on a nitrogen adsorption-and-desorption method.

[0012] In order to form the porosity hydrated-alumina layer which has the above pore structures, it is desirable to add a binder to an alumina sol preferably, to consider as the shape of a slurry, to apply on a base material using a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a comma coating machine, etc., and to adopt the method of drying.

[0013] As a binder, the organic substance, such as starch, its denaturation object, polyvinyl alcohol and its denaturation object, an SBR latex, an NBR latex, a hydroxy cellulose, and a polyvinyl pyrrolidone, can be used. Since it has a possibility that the intensity of a porosity hydrated-alumina layer may become inadequate when there is little amount of the binder used, and it has a possibility that the absorbed dose of ink and the amount of support of coloring matter may become low when there is conversely, about 5 - 50% of the weight of its hydrated alumina is desirable. [too much]

[0014] Since porosity hydrated-alumina layer thickness has a possibility that coloring matter cannot be supported enough but only the low printed matter of the depth of shade may be obtained when it is too thin, it is not desirable. Conversely, since the intensity of a porosity hydrated-alumina layer falls or there is a possibility that transparency may decrease and the transparency or texture of printed matter may be spoiled when too thick, it is not desirable. The thickness with a desirable porosity hydrated-alumina layer is 1-50 micrometers.

[0015] The transparent poly membrane in this invention is formed in the front face of the above-mentioned porosity hydrated-alumina layer, and covers this. This transparent poly membrane has the effect which raises the water resistance of a picture, and weatherability. Transparence means that the picture formed in the porosity hydrated-alumina layer can observe through a poly membrane here. Although it is desirable that it is colorlessness, you may color in order to give design nature. Especially the quality of the material of a transparent poly membrane is not limited, but can use various polymeric materials. Moreover, in the range which does not spoil transparency, even if the filler etc. is blended, it does not interfere.

[0016] The thickness of a transparent poly membrane has desirable 0.5-30 micrometers. When the thickness of a transparent poly membrane does not fulfill 0.5 micrometers, the effect of water resistance and weatherproof improvement is not enough,

and since there is a possibility that quality of image may deteriorate by the manifestation of the interference color, it is not desirable. Since the effect of more than it, water resistance, and weatherproof improvement not only does not increase, but quality of image deteriorates with a concealment of a transparent poly membrane or there is a possibility that peeling of a transparent poly membrane and curl of a record object may occur when the thickness of a transparent poly membrane exceeds 30 micrometers, it is not desirable. The more desirable thickness of a transparent poly membrane is 2-10 micrometers.

[0017] The method of applying the paint which does not contain a pigment component in a porosity hydrated-alumina layer substantially after image formation, i.e., the paint which becomes a transparence result, as an example of a means to form a transparent poly membrane is mentioned. As a paint, various things, such as an oil paint, a fiber system derivative paint, synthetic coating material, and a fluororesin paint, can be used. It is the point which make image formation spread and does not make [it is / a picture / sufficient for and] it it especially to what used water color ink, and the paint which uses oily solvents, such as an oil paint, is desirable.

[0018] As for the resinous principle in a paint, it is desirable that it is 3 - 30 % of the weight. when not filling the resinous principle in a paint to 3% of the weight, the transparent poly membrane formed is thin and the effect of water resistance and weatherproof improvement is enough -- since there is a possibility of it not coming out and producing deterioration of the quality of image by the manifestation of the interference color, it is not desirable On the contrary, since the viscosity of a paint rises, a uniform application becomes difficult, when the resinous principle in a paint exceeds 30 % of the weight and there is a possibility that quality of image may deteriorate, it is not desirable. Since the solvent in a paint is absorbed by the porosity hydrated alumina and viscosity rises at the time of an application in order to form a paint film in a porosity hydrated-alumina layer front face especially in the case of this invention, an application becomes difficult when a resinous principle exceeds 30 % of the weight.

[0019] Especially as for the method of application of a paint, brush coating, spray coating, roller coating, etc. are not limited. An air drying is sufficient as dryness and it may be heated if needed.

[0020] After recording with an ink jet printer etc. as means forming of a transparent poly membrane using the record sheet which formed the porosity macromolecule layer beforehand on the porosity hydrated-alumina layer on a base material in addition to the above applying methods, the method of turning a porosity macromolecule layer precisely and forming a transparent poly membrane on a porosity hydrated-alumina layer is also employable. At this time, ink permeates to a porosity hydrated-alumina layer through a porosity macromolecule layer, and a hydrated-alumina layer is fixed to it, and it forms a picture. As a means of precise-izing of a porosity macromolecule layer, heat-treatment is desirable.

[0021] An example of the record sheet used for this method is shown in drawing 1. The porosity hydrated-alumina layer 2 is formed in the base material 1, and the laminating of the porosity macromolecule layer 3 is carried out further. When using such a record sheet, even if it does not use a paint etc. after record, there is an advantage that the record object with which the transparent poly membrane was formed can be obtained.

[0022] As for a porosity macromolecule layer, it is desirable to carry out application dryness and to form a macromolecule latex on a porosity hydrated-alumina layer. As a macromolecule latex, it is independent, or a PVC latex, an SBR latex, an NBR latex, etc. can be mixed and used.

[0023] As for a macromolecule latex, it is desirable that it is 0.05-0.5 micrometers of mean particle diameters. When the mean particle diameter of a macromolecule latex does not fulfill 0.05 micrometers, the good porosity macromolecule layer of absorptivity and permeability of ink is not formed, enough, ink permeates, a porosity hydrated-alumina layer is not fixed to it, and a desired picture cannot be formed. When the mean particle diameter of a macromolecule latex exceeds 0.5 micrometers, there is a possibility that the dot of ink may become uneven and the fall of a picture may arise. A mean particle diameter more desirable than a macromolecule latex is 0.08-0.3 micrometers.

[0024] As for the coat formation minimum temperature of a macromolecule latex, it is desirable that it is in the range of 50-150 degrees C. When the coat formation minimum temperature heats the paint film of a macromolecule latex, it is minimum temperature which can coat-ize this uniformly. In this invention, although it does not become a precise coat in order to make it a porosity macromolecule layer after applying a macromolecule latex, it is necessary to carry out stoving to a grade with a fixed mechanical strength on conditions which a latex particle combines. If it is difficult to obtain a porosity macromolecule layer that it is easy to become a precise coat and it tends to prevent this in case a macromolecule latex is applied and it dries, when the coat formation minimum temperature does not fulfill 50 degrees C, the drying time will become long, and since it is not industrial, it is not desirable. Since it is necessary to make high heat treatment temperature after image formation and there are decomposition of a macromolecule, a problem of coloring, and a problem of the thermal denaturation of a base material or coloring matter when the coat formation minimum temperature exceeds 150 degrees C, it is not desirable. The more desirable coat formation minimum temperature is 65-130 degrees C.

[0025] Porosity macromolecule layer thickness has desirable 0.1-10 micrometers. when thickness does not fulfill 0.1 micrometers, the water resistance when coat-izing and the effect of weatherproof improvement are enough -- since there is a possibility of it not coming out and causing deterioration of the quality of image by the manifestation of the interference color, it is not desirable Since the absorptivity of ink falls, or quality of image deteriorates when a crack occurred and coat-izes or there is a possibility that the effect of water resistance and weatherproof improvement may not occur when thickness exceeds 10 micrometers, it is not desirable. 0.3-5 micrometers of more desirable thickness of a porosity macromolecule layer are 0.5-3 micrometers especially preferably.

[0026] Although especially the solid-content concentration of a macromolecule latex is not restricted, the latex of 1 - 50% of the weight of solid-content concentration can be used suitably. In addition, to a macromolecule latex, you may add other macromolecule components with a binder operation.

[0027] Especially the method of application of a macromolecule latex is not restricted, but can use a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a gravure coating machine, etc. It is desirable to perform dryness at the temperature below the coat formation minimum temperature of the macromolecule latex to be used.

[0028] Thus, when a picture is formed in the formed record sheet with the upper shell ink jet printer of a porosity macromolecule layer, ink reaches it to a hydrated-alumina layer through a porosity macromolecule layer. Since the

adsorptivity of a hydrated alumina of the coloring matter in ink is high, a picture is substantially formed in the portion of a hydrated-alumina layer. Then, if a porosity macromolecule layer is made precise with heat treatment etc., it will come to act as a protective layer of the coloring matter to which the rarefaction was carried out and the hydrated-alumina layer was fixed. That heat treatment should just be more than the coat formation minimum temperature of a latex, especially a heating means is not restricted but hot blast, an iron, etc. can be used for it.
[0029] Furthermore, since the beading-proof property at the time of recording with an ink jet printer improves remarkably when the different-species particle is distributing in the porosity macromolecule layer, it is desirable. As a particle, an inorganic particle is desirable and a silica particle is specifically suitable. If a size and loadings are suitable for this particle, when a porosity macromolecule layer is turned precisely, it will not spoil transparency.
[0030] When using a silica particle, as a diameter of a particle, about 0.03-0.3 micrometers is suitable. Since the above-mentioned effect is not discovered enough when a particle diameter does not fulfill 0.03 micrometers, it is not desirable. Since there is a possibility of transparency being insufficient and degrading quality of image when a particle diameter exceeds 0.3 micrometers, and a porosity macromolecule layer is turned precisely, it is not desirable. A more desirable particle diameter is 0.05-0.1 micrometers.
[0031] When using a silica particle, as for the mixed rate of a macromolecule and a silica particle in a porosity macromolecule layer, it is desirable that a silica particle is 50 or less % of the weight to the total quantity of a macromolecule and a silica particle. Since it is difficult to carry out the precise rarefaction after record when a silica particle exceeds 50 % of the weight, it is not desirable. The silica particle of a more desirable rate is 15 - 40 % of the weight to the total quantity of a macromolecule and a silica particle.
[0032] The method of preparing the coating liquid which mixed the silica sol to the macromolecule latex as a method of obtaining the porosity macromolecule layer of composition of the silica particle having distributed uniformly, and carrying out application dryness of this on a hydrated-alumina layer is suitable. In this case, a silica particle also has the effect which suppresses generating of a crack in the case of formation of a porosity macromolecule layer. The method of application etc. can adopt the same thing as a latex independent case. Porosity macromolecule layer thickness is the same as a latex independent case, and good.
[0033] In case the precise rarefaction is carried out even if it blends different-species particles, such as a silica, and does not carry out when a macromolecule latex is applied and a porosity macromolecule layer is formed, layer thickness hardly changes. That is, although it is porosity, it is thought that the porosity macromolecule layer with small pore volume is formed. For this reason, when it heats, it is thought that a particle welds easily and carries out the rarefaction.
[0034] The glossiness of a record object improves by forming a transparent poly membrane. When paper is especially used as a base material, and glossiness improves, improvement in quality of image is also found. Since it has gloss good from the first when plastic film smooth as a base material is used, glossiness becomes high too much, depending on the use of a record object, texture is conversely bad and there may be things. In such a case, lusterless processing can also be performed to a transparent poly membrane.
[0035] Although the record object of this invention is suitable when recording especially using an ink jet printer, it is applicable to other recording methods recorded using coloring matter.
[0036]
[Function] They are the oxygen in air, ozone, and NOx in that coloring matter touches water in this invention when a transparent poly membrane covers a porosity hydrated-alumina layer ****. It reacts, or prevents volatilizing and has the function which covers ultraviolet rays further. Since the transparent poly membrane side of a hydrated-alumina layer is mostly fixed to coloring matter even if it penetrates air etc. like [in case base materials are paper and cloth], an effect is demonstrated similarly.
[0037]
[Example] Example 1.
32g of 6.2 % of the weight solution of polyvinyl alcohol was mixed with alumina-sol of 18 % of the weight of solid contents compounded by hydrolysis and amalgam-decomposition method of aluminum alkoxide 100g, and it considered as coating liquid. On the polyethylene-terephthalate film (a white film, 125-micrometer **), coating of this coating liquid was carried out using the bar coating machine so that the coating thickness after dryness might be set to 30 micrometers. It heat-treated at 140 degrees C, and the record sheet took after drying this.
[0038] After using the ink jet printer (CJ[by Canon, Inc.]-10 type) for this record sheet and forming a picture in it, what diluted the synthetic coating material (urethane varnish by Kansai Paint Co., Ltd.) of an urethane system with petroleum system thinner to 20 % of the weight of pitches was applied with the brush, was air-dried, the transparent poly membrane with a thickness of about 5 micrometers was formed, and the record object was obtained.
[0039] Example 2.
After recording on the record sheet of an example 1 with an ink jet printer similarly, n-butanol solution of 5 % of the weight of polyvinyl butyral resin was used as the paint, application dryness was carried out like the example 1, the transparent poly membrane with a thickness of about 5 micrometers was formed, and the record object was obtained.
[0040] Example 3.
On the record sheet of an example 1, it applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 2 micrometers by 0.1 micrometers of mean particle diameters in the PVC latex (the Nippon Zeon Co., Ltd. make, tradename G351) of 10 % of the weight of solid contents, and stoving was carried out in 60-degree C atmosphere, and the porosity macromolecule layer was formed.
[0041] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (100 degrees C), the porosity macromolecule layer was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 2 micrometers.
[0042] Example 4.
On the record sheet of an example 1, it applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 1 micrometer by 0.12 micrometers of mean particle diameters in the SBR latex (the Nippon Zeon Co., Ltd. make, tradename NIPORU LX382) of 5 % of the weight of solid contents, and stoving was carried out in 90-degree

C atmosphere, and the porosity macromolecule layer was formed.
[0043] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (130 degrees C), the porosity macromolecule layer was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 1 micrometer.
[0044] Example 5.
The silica sol (catalyst Chemicals industrial incorporated company make, tradename KATAROIDO SI-80P) of 0.08 micrometers of mean particle diameters was mixed with the SBR latex (the Nippon Zeon Co., Ltd. make, tradename NIPORU LX382) of 5 % of the weight of solid contents at a rate of 80:20 by 0.12 micrometers of mean particle diameters at the solid-content weight ratio, and coating liquid of the 10 % of the weight of the total solid-content concentration was prepared. With time, this mixed coating liquid was not seen but that of especially change was stable. On the record sheet of an example 1, this coating liquid was applied so that a bar coating machine might be used and the thickness at the time of dryness might be set to 1.5 micrometers, stoving was carried out in 90-degree C atmosphere, and the porosity macromolecule layer which the silica particle contained was formed.
[0045] After using the ink jet printer (iris company make) for this record sheet and forming a picture, by heat-treating by hot blast (130 degrees C), the porosity macromolecule layer was turned precisely, the transparent poly membrane was formed, and the record object was obtained. The thickness of a transparent poly membrane was 1.5 micrometers.
[0046] The example of printing.
About these record objects, water resistance and weatherability were evaluated as follows. A result is shown in Table 1 by making into the example of comparison the record object obtained similarly except not forming a transparent poly membrane. water resistance -- a record object -- dead water -- it was immersed in inside for one day, and ** and the thing to which quality of image fell remarkably were evaluated for what has bleeding O and a little in some which are completely changeless as x Weatherability exposed the record object indoors for three months, and evaluated as x ** and the thing which changed brown for what discolored O and a little what does not change at all about the discoloration degree (fade : black shell brown) of the black Records Department.
[0047]
[Table 1]

	耐水性	耐候性
実施例 1	○	○
実施例 2	○	○
実施例 3	○	○
実施例 4	○	○
実施例 5	○	○
比較例	△	×

[0048]
[Effect of the Invention] The record object of this invention is excellent in water resistance and weatherability, and has the preservation stability which maintains high definition over a long period of time. Especially, it is suitable to the record using water color ink. Moreover, the record method of this invention also has the effect that desirable gloss can be given to a record object.
[Brief Description of the Drawings]
[Drawing 1] Explanatory drawing showing the composition of one example of the record sheet of this invention.
[Description of Notations]
1: Base material.
2: Porosity hydrated-alumina layer.
3: Porosity macromolecule layer.

[Translation done.]